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# On the Anionic Preparation of Poly ($\alpha$-methyl styrene)

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Monodisperse poly($\alpha$-methyl styrene) was prepared by the technique of anionic polymerization, in which *n*-butyl lithium, $\alpha$-methyl styrene tetramer or sodium-naphthalene complex was used as initiator and tetrahydrofuran was used as solvent. Experimental procedures for obtaining the polymers with narrow distribution of molecular weight are described in detail.

## 1. INTRODUCTION

Anionic polymerization has been investigated extensively by various investigators to give nearly homogeneous polymers since the discovery by Szwarc[1~11]. According to theoretical studies[12~16], the conditions which lead to the monodisperse polymers are summarized as follows.

(a) *Instantaneous initiation*: the initiation rate should be sufficiently large compared with the propagation rate.

(b) *Absence of depolymerization*: the polymerization reaction should be carried out sufficiently below the *ceiling temperature* so that the depolymerization reaction can be neglected.

(c) *Complete removal of impurities and proper choice of monomer-solvent system*: the presence of impurities and improper choice of monomer-solvent system often lead to such an undesirable reaction as termination or chain-transfer of active ends.

In addition, experiments must be carried out under high vacuum of about $10^{-6}$ mmHg.

In view of the requirements mentioned above and the possibility of making use of the *purging process* which is described later, the combination of $\alpha$-methyl styrene and tetrahydrofuran[8] is considered to be one of the most suitable system to give the monodisperse polymers. This communication presents a detailed description of the method of preparation for monodisperse poly($\alpha$-methyl styrene). In this method, *n*-butyl lithium, sodium naphthalene complex and $\alpha$-methyl styrene tetramer were used as initiator, and tetrahydrofuran was used as solvent. The experimental procedures employed were essentially based on those established by Morton *et al.*[10] and others[6,11], but some modifications were applied at need. The physical properties of the obtained polymers will be described elsewhere[17].

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## 2. EXPERIMENTAL

### a. Vacuum Apparatus

The general scheme of the vacuum apparatus is shown in Fig. 1, which is essentially based on the apparatus of Morton *et al.*[9,10]. But some modifications and simplifications were applied in order to achieve high vacuum more smoothly. The main line was constructed with hard glass of 20 mm diameter and the cocks C were used with high vacuum electron grease (Soh Electronics Co., Ltd.).

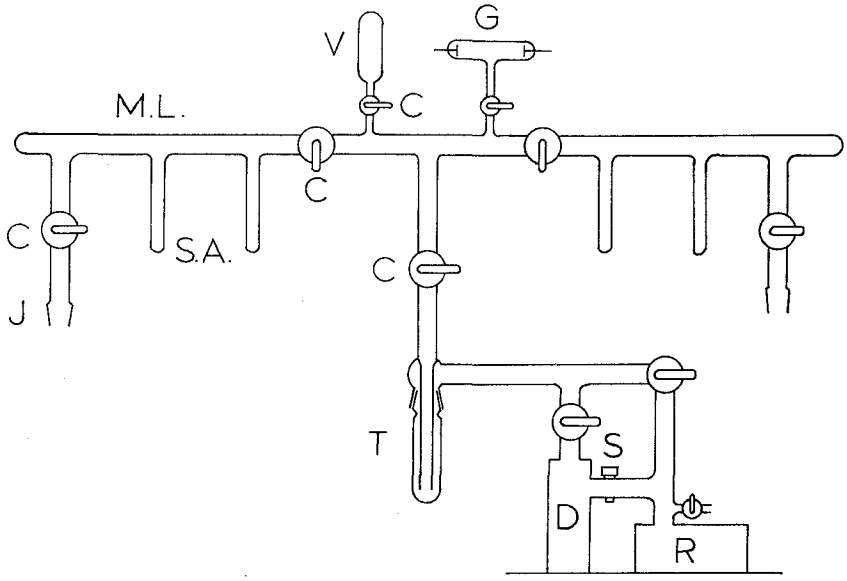


Fig. 1. General scheme of the vacuum apparatus.

The main line (M.L.) and side arms (S.A.) were pumped out to $10^{-6}$ mmHg by a rotary pump R and an oil diffusion pump D through a trap T which was cooled by liquid nitrogen. The degree of vacuum was checked by a hot cathode ionization vacuum gauge* combined with a vacuum tube V.

Almost all operations were carried out on the side arms. Absence of pin holes was carefully checked in every operation by a Tesla coil or a gas-tube sign transformer combined with a Geissler's tube G. Preliminarily washed and cleaned with cromic acid mixture and distilled water, the preparation apparatus was attached to the vacuum line and flamed by a hand burner carefully to exclude water absorbed on the inner surface of glass.

### b. Purification of Solvents

Benzene and ether were used as solvent in the preparation of *n*-butyl lithium. *n*-Hexane was used as diluent of *n*-butyl lithium. Tetrahydrofuran was used as solvent in the polymerization and as diluent of $\alpha$-methyl styrene tetramer or sodium-naphthalene complex.

* This gauge is more suitable for high vacuum measurement than the MacLeod gauge because of its higher sensitivity in the range of $10^{-3}$~$10^{-7}$ mmHg.

(i) **Benzene and *n*-Hexane.** The purification procedure is nearly the same in both cases, so the preparation of *n*-hexane is mainly described. *n*-Hexane was preliminarily purified by passing it through an alumina column to remove peroxides and then rectified over sodium metal. The purification in vacuum was carried out through a series of apparatus shown in Fig. 2, in which cocks were removed as much as possible. Flask $F_0$, containing distilled *n*-hexane and a few pieces of sodium metal was attached by a universal joint J to a side arm shown in Fig. 2(a).

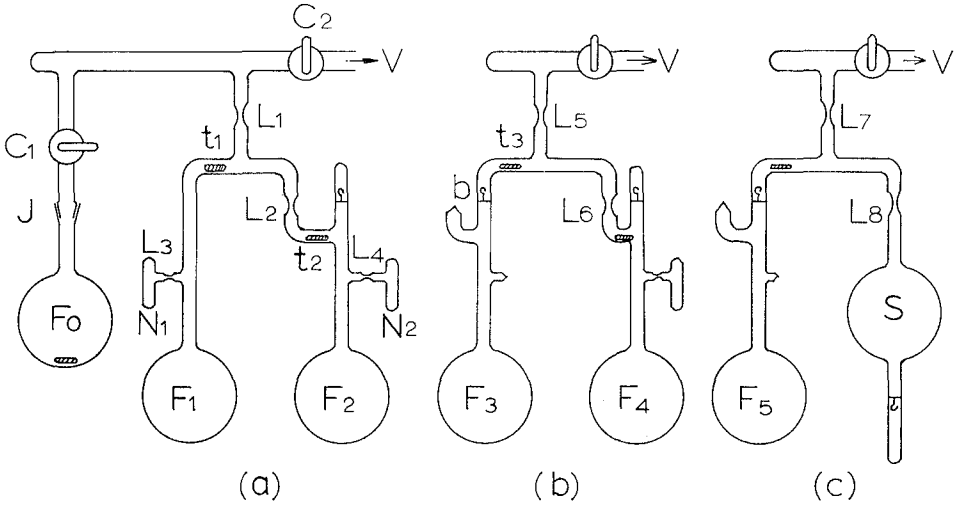


Fig. 2. Apparatus for preparation of solvents.

*n*-Hexane was degassed at −78°C cooled with dry ice-methanol mixture* and was magnetically stirred at room temperature for several hours. This cycle was repeatedly continued until metallic surface was observed on sodium metal.

Next, sodium-potassium alloy was melted into flask $F_1$ from capsule $N_1$ containing the both metals, and sodium mirror was produced on the inner surface of flask $F_2$ by the vacuum evaporation coating of sodium metal from capsule $N_2$ under $10^{-6}$ mmHg. These two operations must be proceeded simultaneously to obtain the clean surfaces of the alloy and mirror. *n*-Hexane in flask $F_0$ was subsequently distilled into flask $F_1$, cooled with dry ice-methanol mixture, and repeatedly degassed and stirred with a magnetic tip $t_1$ to make the solvent contact always with new surfaces of the molten alloy. Then, the apparatus was sealed off at $L_1$ from the vacuum line under vacuum.

Finally, *n*-hexane was distilled into flask $F_2$ having a breakable seal, and continuously stirred for about one day after the flask $F_2$ was cut off from the vacuum line. When the sodium mirror of flask $F_2$ was consumed to some degree, flask $F_2$ was again connected to the vacuum line as illustrated in Fig. 2(b) as flask $F_3$. A new sodium mirror was prepared in flask $F_4$ under $10^{-6}$ mmHg. Then, immediately after the breakable seal b was crushed by a magnetic tip $t_3$, the assembly of flasks $F_3$ and $F_4$ was cut off under vacuum from the vacuum line at $L_5$. During

* In the case of benzene, the volume of liquid should be no more than one half of the capacity of flask $F_0$ to avoid destruction of this flask caused by the expansion of benzene in the course of warming.

these operations, flask $F_3$ must be kept at about $-70°C$. Finally, *n*-hexane was distilled into flask $F_4$. These processes were repeatedly applied until no consumption of sodium mirror was observed. *n*-Hexane was stored in a flask with clean mirror, and before use, it was transferred by distillation into a new flask S as shown in Fig. 2(c).

**(ii) Tetrahydrofuran and Ether.** Tetrahydrofuran (THF), after removal of peroxides through alumina, was rectified over sodium metal and stirred magnetically with a piece of sodium metal and a small amount of benzophenone in isolation from air for a few days until purple color was observed*. Flask $F_0$, containing colored THF, was jointed to the vacuum line as shown in Fig. 2(a), where THF was repeatedly degassed at $-78°C$ (dry ice-methanol mixture) and stirred at room temperature until no bubbling of gas was detected and no color change was observed. Then, sodium mirrors were simultaneously created in flasks $F_1$ and $F_2$ under high vacuum, and THF was carefully distilled from flask $F_0$ to flask $F_1$ except for the initial and last parts of distillate. Finally the assembly of flasks $F_1$ and $F_2$ was cut and sealed off at $L_1$ under vacuum.

Tetrahydrofuran distilled in flask $F_1$ was stirred at room temperature and then distilled into flask $F_2$ slowly so as to remove excess benzophenone contained in THF. Such a distillation through sodium mirror was repeatedly carried out in the apparatus shown in Fig. 2(b) until no colored complex was produced**. Finally, THF purified by the apparatus shown in Fig. 2(c) was sealed in flask S having a breakable seal and stored in a refrigerator.

The presence of benzophenone in THF, though a very small amount, makes the initiator inactive in the polymerization of $\alpha$-methyl styrene which is initiated by *n*-butyl lithium in THF. Thus, a modification of the purification process of THF was attempted in which use of benzophenone was avoided. In the step corresponding to Fig. 2 (a), the test of purification of THF was made only by observation of the metallic surface on sodium tips without using benzophenone. In the steps of Figs. 2(b) and 2(c), the end of the purification process was determined by the appearance of light blue color which is due to sodium mirror and pure THF.

**c. Purification of $\alpha$-Methyl styrene**

$\alpha$-methyl styrene, which was preliminarily washed with dilute aqueous solution of sodium hydroxide to remove the polymerization inhibitor and stored over calcium chloride for several days to remove water, was refluxed and distilled with calcium hydride under reduced pressure. Then, the middle part of this distillate was sealed in a flask, which has a breakable seal and contains a large amount of calcium hydride.

The purification of $\alpha$-methyl styrene in vacuum was attempted by using several reagents, *i.e.*, (1) calcium hydride, (2) initiator itself, and (3) sodium-potassium alloy or sodium mirror. Of these reagents, the last one (3) was found to be most appropriate for the purpose. Thus, the process by the third reagent is here de-

* Naphthalene, anthracene and benzophenone produce colored complex compound (radical anion) with sodium in THF, respectively, if there is no impurity such as water, oxygen, carbon dioxide, peroxides and so on. In the case of ether, a green color will be observed.

** The sodium mirror is melted in THF if there is benzophenone even in a very small amount.

scribed in detail. As shown in Fig. 3 (a), flasks M containing $\alpha$-methyl styrene and calcium hydride were attached to the apparatus which consists of flask $F_1$ and receivers $F_3$ and $F_4$. $F_3$ and $F_4$ were flamed under vacuum, and calcium hydride was introduced into flask $F_1$ through $N_1$. The whole apparatus was evacuated to $10^{-6}$ mmHg with calcium hydride flaming and then cock $C_1$ was closed. $\alpha$-Methyl styrene was poured into flask $F_1$ by crushing a breakable seal b with a magnetic tip t and was frozen by dry ice-methanol mixture and then degassed by opening cock $C_1$. Flask $F_1$ was subsequently warmed to room temperature and stirred with calcium hydride for a few hours. The degassing and stirring were repeatedly carried out until no emergency of gas was observed. After a small amount of $\alpha$-methyl styrene was distilled and sealed in flask $F_3$ as initial distillate, almost all the monomer was distilled, with warming flask $F_1$ above the ceiling temperature of $\alpha$-methyl styrene, into flasks $F_4$ and sealed off under $10^{-6}$ mmHg.

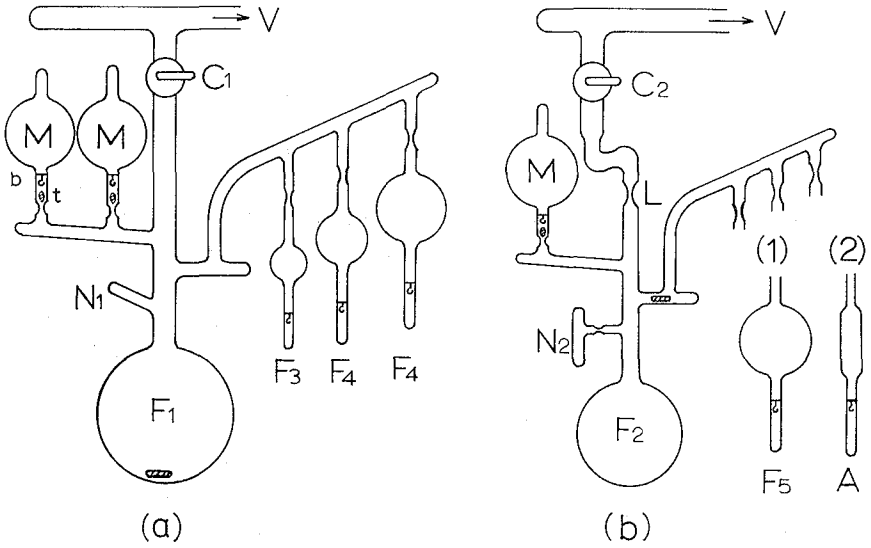


Fig. 3. Apparatus for preparation of $\alpha$-methyl styrene.

Next, one of these flasks $F_4$ was attached to the apparatus shown in Fig. 3 (b) as indicated by M. Purification was carried out by the same way as that mentioned in the step of Fig. 3 (a), except that sodium-potassium alloy or sodium mirror was used in place of calcium hydride and that the lower part L was cut off from the vacuum line before the distillation. The distillation of $\alpha$-methyl styrene was carried out in the sealed system from flask $F_2$ to flask $F_5$. This purification was repeated several times and finally $\alpha$-methyl styrene was sealed in ampoules A through sodium mirror. These ampoules were stored under refrigeration.

**d. Preparation of Initiators**

(i) ***n*-Butyl Lithium.** *n*-Butyl lithium (*n*-BuLi) was prepared by the reaction between *n*-butyl bromide (*n*-BuBr) and metallic lithium in ether[11] : $C_4H_9Br + 2Li \longrightarrow C_4H_9Li + LiBr$.

The reaction apparatus was shown in Fig. 4, where flasks B and C contain purified benzen and ether, respectively, and ampoule D contains *n*-BuBr purified

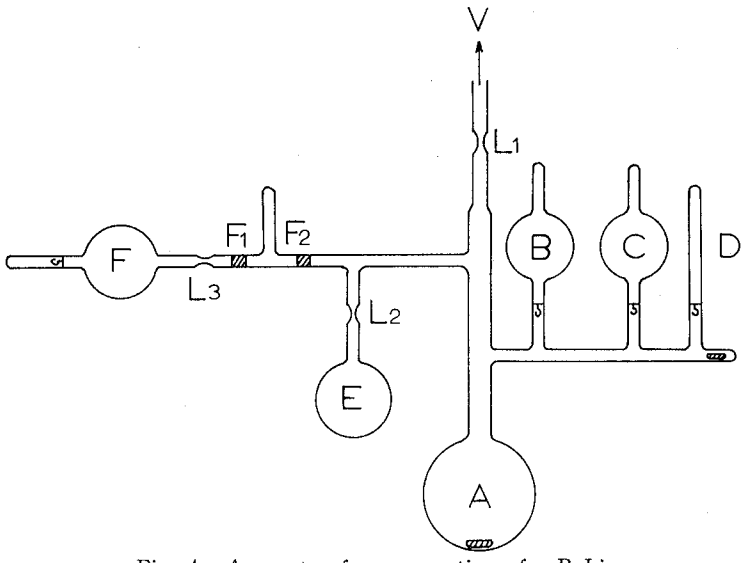


Fig. 4. Apparatus for preparation of *n*-BuLi.

by the distillation with calcium hydride. After metallic lithium was placed in the reactor A, the apparatus was evacuated to $10^{-6}$ mmHg and sealed off at $L_1$. Ether and *n*-BuBr were added to A and reacted with metallic lithium at 0~10°C for several hours, and then benzene was added to precipitate lithium bromide (LiBr) which was a by-product of this reaction. From the reaction mixture, ether was thoroughly removed to flask E and cut off at $L_2$. Then, benzene solution of the initiator was carefully transfered to flask F by decantation through glass filters $F_1$ and $F_2$ so as not to move the precipitate of LiBr as far as possible, and finally the flask F was sealed at $L_3$. Since LiBr is soluble in ether and almost insoluble in benzene, the complete removal of ether before the decantation may promise the absence of $Br^-$ in the initiator solution in flask F. The existence of $Br^-$ is, however, extremely undesirable[11,18]. Therefore, the initiator solution was further repeatedly filtered after the storage of a long period under refrigeration which permits the growth of LiBr crystal if it remained in solution.

The original solution of this initiator has a yellow orange color and was stored in the refrigerator. The dilution of *n*-BuLi* was carried out by the apparatus shown in Fig. 5, which was pumped to $10^{-6}$ mmHg and sealed at L. A small part of the original solution of *n*-BuLi in flask I and *n*-hexane in flask D purified mentioned above were mixed with each other and sealed** in ampoules A, B and C whose volumes were already determined. A initiator solution with desirable concentration of *n*-BuLi was prepared by repeating such a dilution, and finally it was stored in small ampoules A shown in Fig. 5 under refrigeration.

* Since *n*-BuLi is surprisingly sensitive to and becomes inactive by heat, flask I containing *n*-BuLi solution should be cooled well and taken care not to be exposed to the flame. The death of *n*-BuLi is known by the white turbidity of its solution caused by decomposite products of *n*-BuLi.

** The cut off in ampoules must be carried out by a small flame of burner immediately after the parts L were well washed with solvent by cooling there with dry ice-methanol mixture. Ampoules, A, B and C must be kept sufficiently cool during the process.

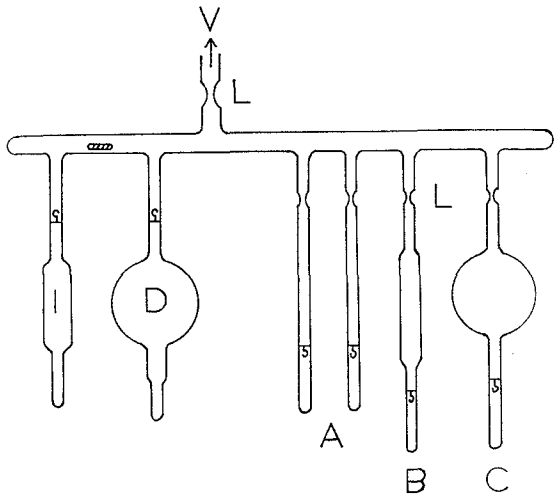


Fig. 5. Apparatus for the dilution of initiators and terminators.

**(ii) $\alpha$-Methyl styrene Tetramer and Sodium-naphthalene Complex**[3,6,19~21]. The production of sodium-naphthalene complex and the dimerization of the radicals, which occurred by the addition of $\alpha$-methyl styrene to sodium-naphthalene complex solution, are slow reactions. Therefore, these reactions require much longer time than the preparation of *n*-BuLi does.

The apparatus of preparation was shown in Fig. 6. After sodium mirror was made in flask B by vacuum evaporation of sodium metal in capsule E, the apparatus was sealed at $L_2$ under $10^{-6}$ mmHg. THF in flask D, which contained naphthalene, was distilled into flask B and stored until a permanent dark green color due to sodium-naphthalene complex was observed. Flask A was washed with colored THF repeatedly and then $\alpha$-methyl styrene in flask C was distilled into flask B. The green color in flask B then changed to red gradually. The apparatus

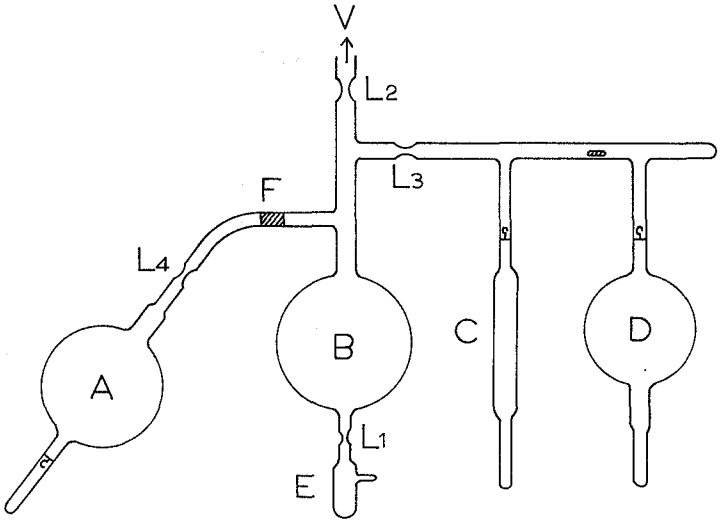


Fig. 6. Apparatus for preparation of $\alpha$-methyl styrene tetramer and sodium-naphthalene complex.

was left untouched for a week in order to ripen $\alpha$-methyl styrene tetramer, and then the final initiator solution was decanted through a glass filter F and sealed in flask A. The original solution was diluted with THF in the similar way as that of *n*-BuLi by using the apparatus shown in Fig. 5.

**e. Determination of the Concentration of Initiator Solutions**

(i) **Titration Method**[22~24]. The titration in vacuum was not adopted because of its technical difficulties. The titration was carried out with a standard acid solution, where *n*-BuLi was killed in air by water and the alkaline quantity produced was determined from the neutral point of the titration curve obtained by a pH meter. Use of pH meter was suitable for the titration of the present system, for which the color change of ordinary indicator was quite obscure because of the turbidity of the killed initiator solution.

(ii) **Optical Method**[25~27]. The optical method based on the absorption spectrum was most conveniently used for determining the concentration of the dilute initiator solution. A special quartz cell was used for this purpose, which was 2 mm thick, 10 mm wide and contained a spacer about 1.9 mm thick. The molar absorption coefficient of *n*-BuLi-THF solution containing about 5% of *n*-hexane was log $\varepsilon=1.5$ for the light of the wave length $\lambda=300$ m$\mu$*. Measurements were made by Hitachi Optical Photometer in the concentration range of $10^{-5}\sim10^{-6}$ mole *n*-BuLi/cc, where the solution was colored slightly pale yellow.

**f. Preparation of Terminators**

Water, methyl alcohol, ethyl alcohol and *n*-butyl alcohol were used as terminating agent for the polymers. The preparation of *n*-butanol (*n*-BuOH) will be briefly described here.

*n*-Butanol, which was treated with sodium bisulfite solution to remove bases, aldehydes and ketones, was fractionally distilled after drying over magnesium metal powder. A flask containing *n*-BuOH and calcium hydride, was attached to the vacuum line as shown by A in Fig. 7. *n*-BuOH was repeatedly degassed under

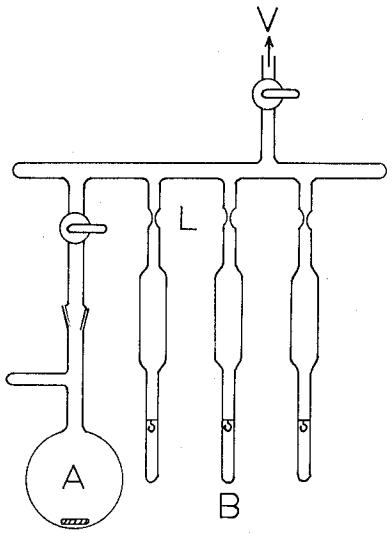


Fig. 7. Apparatus for preparation of terminator, *n*-BuOH.

* *n*-BuLi displays no discrete band and shows only the increasing end absorption in THF-*n*-hexane mixture[25].

$10^{-6}$ mmHg at $-78°C$ and stirred with calcium hydride until the bubbling of gas was completely run out. Then, *n*-BuOH was distilled into ampoules B and sealed under vacuum.

The dilution of *n*-BuOH was carried out by the apparatus shown in Fig. 5 and finally sealed in small ampoules A. In this case, THF was used as diluent because THF was the solvent of the polymerization.

**g. Polymerization**

Polymerization[11] was carried out in the apparatus shown in Fig. 8, where THF, *n*-BuLi (initiator), $\alpha$-methyl styrene and *n*-BuOH (terminator) were sealed in

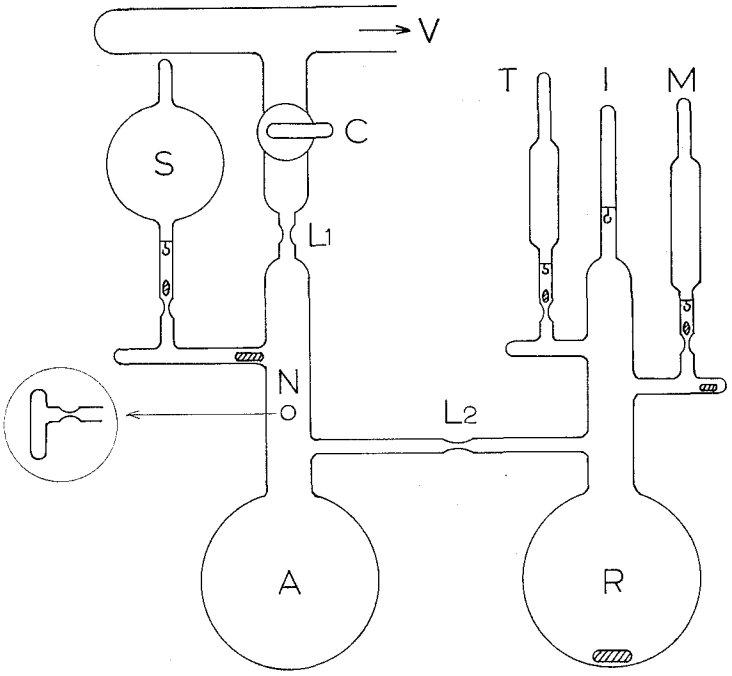


Fig. 8. Apparatus for polymerization.

flask S, ampoules I, M and T, respectively. After the whole apparatus was pumped to $10^{-6}$ mmHg under flaming*, and after a fine sodium mirror was made in flask A by the vacuum evaporation of sodium metal from capsule N, cock C was closed, and THF was introduced from flask S into flask A which was cooled with dry ice-methanol mixture at $-78°C$. Flask S was then cut off and the whole apparatus was degassed under cooling and sealed off at $L_1$. THF was magnetically stirred in flask A and the reaction flask R was washed with THF by cooling every part of it with dry ice-methanol mixture. Then, THF was returned and stirred in flask A. After this cleaning was repeated several times, THF was carefully distilled in vacuum into flask R and finally the reactor was sealed at $L_2$.

In the polymerization process, $\alpha$-methyl styrene was first added from ampoule M to R and mixed well with THF. Then, *n*-BuLi contained in ampoule I was

* The ampoule I containing the initiator solution should be cooled with cold asbest tapes, for example, so as not to be touched or heated by the flame.

added to R and stirred vigorously. The solution was colored clear red at this stage. A small amount of $\alpha$-methyl styrene and $n$-BuLi, which remained in ampoules I, M and other parts of the apparatus, were washed into reactor R with THF. The solution in R was stirred vigorously at room temperature[19,20,28,29] to stimulate the so-called *"purging"* process of impurity*, ane then it was immersed in the dry ice-methanol mixture (−78°C)**. Polymerization was proceeded under continuous stirring for a few hours or days***. Finally, $n$-butanol in ampoule T was introduced into R to kill the living ends of polymers. The reaction product was poured into methanol containing a small amount of distilled water, and the precipitates obtained was repeatedly washed with methanol.

**h. Purification and Storage of Samples**

Polymer samples obtained were purified preliminarily by the repeated precipitation from the dilute benzene solutions into methanol. Then, the polymers were fractionated by a large scale of Desreux column[30] at 25°C, in which ethanol and benzene were used as precipitant and solvent, respectively.

The column fractionation was adopted to remove low molecular weight components which were often involved as impurities though to a very small amount. The middle part in the fractionates was freeze-dried from benzene solution, followed by evacuation under reduced pressure for about 24 hours at 60°C. Then, the samples obtained were sealed in ampoules under $10^{-6}$ mmHg and stored in the refrigerator, because the stability of poly($\alpha$-methyl styrene) in air is not guaranteed[31].

## 3. ACKNOWLEDGEMENTS

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## REFERENCES

(1) R. Milkovich, M. Szwarc and M. Levy, *J. Am. Chem. Soc.*, **78**, 2656 (1956).
(2) M. Szwarc, *Makromol. Chem.*, **35**, 132 (1959).
(3) J.E. Mulvaney, C.G. Overberger and A.M. Schiller, *Fortschr. Hochpolym. Forsch.*, **3**, 106 (1961).
(4) M. Szwarc, *Proc. Royal Soc. London*, **A 279**, 260 (1964).
(5) R. Asami, *Kobunshi (Polymer)*, in Japanese, **14**, 548 (1965).
(6) F. Wenger, *J. Am. Chem. Soc.*, **82**, 4281 (1960).
(7) F. Wenger and S.P.S. Yen, *Makromol. Chem.*, **43**, 1 (1961).
(8) F. Wenger, *Makromol. Chem.*, **64**, 151 (1963).
(9) M. Morton, R. Mildovich, D.B. McIntyre and L.J. Bradley, *J. Polymer Sci.*, **A1**, 443 (1963).

* Detailed mechanism of the purging process is not fully established. But, in this process, impurities if remained are consumed before the propagation reaction is started by cooling to −78°C. This is necessary to obtain the monodisperse distribution of the polymerized $\alpha$-methyl styrene.

** Polymerization of $\alpha$-methyl styrene in THF, using $n$-BuLi as initiator, should be carried out at −78°C to avoid the reaction between $n$-BuLi and THF; $n$-BuLi may activate THF to oxide anion by a ring opening reaction.

*** The polymerization time must be carefully determined, depending on the concentration of the initiator solution[3].

(10) M. Morton, A.A. Rembaum and J.L. Hall, *J. Polymer Sci.*, **A1**, 461 (1963).
(11) T. Fujimoto, N. Ozaki and M. Nagasawa, *J. Polymer Sci.*, **A3**, 2259 (1965).
(12) P.J. Flory, *J. Am. Chem. Soc.*, **62**, 1561 (1940).
(13) L. Gold, *J. Chem. Phys.*, **28**, 911 (1958).
(14) V.S. Nanda and R.K. Jain, *J. Polymer Sci.*, **A2**, 4583 (1964).
(15) V.S. Nanda, *Trans. Faraday Soc.*, **60**, 947, 949 (1964).
(16) B.D. Coleman and T.G Fox, *J. Am. Chem. Soc.*, **85**, 1241 (1963).
(17) M. Abe, K. Sakato, T. Kageyama, M. Fukatsu and M. Kurata, *Bull. Chem. Soc. Japan*, to be published.
(18) K.F. O'Driscoll and A.V. Tobolsky, *J. Polymer Sci.*, **35**, 259 (1959).
(19) D.J. Worsfold and S. Bywater, *J. Polymer Sci.*, **26**, 299 (1957).
(20) D.J. Worsfold and S. Bywater, *Canad. J. Chem.*, **36**, 1141 (1958).
(21) C.L. Lee, J. Smid and M. Szwarc, *J. Phys. Chem.*, **66**, 904 (1962).
(22) H. Gilman, P.D. Wilkinson, W.P. Fishel and C.H. Meyers, *J. Am. Chem. Soc.*, **45**, 150 (1932).
(23) H. Gilman and A.H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).
(24) W.L. Everson, *Anal. Chem.*, **36**, 854 (1964).
(25) R. Waack and M.A. Doran, *J. Am. Chem, Soc.*, **85**, 1651 (1963).
(26) R. Waack and M.A. Doran, *J. Phys. Chem.*, **67**, 148 (1963).
(27) S. Bywater, A.F. Johnson and D.J. Worsfold, *Canad. J. Chem.*, **42**, 1255 (1964).
(28) H.W. McCormick, *J. Polymer Sci.*, **25**, 488 (1957).
(29) A. Vrancken, J. Smid and M. Szwarc, *Trans. Faraday Soc.*, **58**, 2036 (1962).
(30) V. Desreux, *Rec. Trav. Chim. Pays-Bas.*, **68**, 789 (1949).
(31) G.C. Berry, *J. Chem. Phys.*, **44**, 4550 (1966).